

Kinetics of Reduction of Vanadiferous Titanomagnetite ore of Orissa

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ABSTRACT

200 mesh powder of vanadium bearing titaniferous magnetite ore was pelletised to 0.5 cm dia spheres, heat hardened at 1100°C for $\frac{1}{2}$ hour in nitrogen. The pellets were reduced in a calibrated mixture of 60% N₂, 40% CO. The temperature vs weight loss was recorded in a Shimadzu Thermogravimeter model TGA-31 at 900, 955, 999 and 1050°C. The results conformed to Mc Kewan's phase boundary reaction model, yielding an activation energy of 25.5 kcal/mole. No kinetic studies of reduction of titanomagnetite has been reported. The activation energy for magnetite reduction ranges from 13 to 45 kcal/mole as reported in literature. Presence of TiO₂ is known to hinder reduction kinetics of iron oxides. The observed higher activation energy and slower rate of reduction of titanomagnetite has been explained in terms of its spinel structure and preferential positions of metal ions.

Introduction

Vanadium bearing titanomagnetite ore is one of the major sources of vanadium in the world. Titanomagnetite ore of Orissa has drawn considerable attention due to its appreciable vanadium content. The characterisation of the ore is an essential step for determining its grade, economic viability and other features. Dunn and Dey¹ have carried out studies on vanadium bearing titanomagnetite ore of Kumardhubi in Mayurbhanj district of Orissa and adjacent areas. They observed the presence of vanadium maghemite in these ores and suggested the name of this mineral as coulsonite. Mitra and Chatterjee² have also investigated about the presence of different mineral constituents and

their mode of occurrence with particular reference to vanadium content. Their investigation shows that the ore contains magnetite, ilmenite, hematite and limonite. They have also reported that vanadium occurs as an integral part of magnetite lattice substituting to a limited extent the ferric ion species. Roy³ also carried out detailed ore microscopic investigation of these ores and observed the presence of coulsonite replacing magnetite along the octahedral plane of magnetite lattice.

In the present investigation the authors have attempted to characterize the ore by various methods such as ore microscopy, x-ray diffraction, chemical and physical analysis. In the last 30 years a number of new processes for

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the reduction of iron ores has been developed, which differ essentially in the type of fuel used. Some of these processes utilise cheap, low grade coal as reductant prior to smelting in the electric furnace, which reduces the total power consumption. In these processes the reduction of the ore is carried out in the solid state. Therefore the operating temperatures are usually less than 1000°C, not only to prevent melting but also sintering. At these temperatures the reducibility of the ore becomes an important factor, which deserves special attention.

Since data are not available on reduction kinetics of vanadiferous titanomagnetite ore its reduction kinetics was studied and compared with the reduction behaviour of magnetite available in literature.

Experimental

Chemical Analysis

The ore samples were obtained from Kumardhubi village. Three samples were chemically analysed by standard classical methods of analysis.

Density and porosity

The density and porosity of two ore samples have been determined by pycnometric method⁴ using -300 mesh powder. The theoretical density, apparent density and porosity were calculated. The porosity was calculated from theoretical density and apparent density by the following relationship⁴.

$$\% \text{ porosity} = \frac{D_t - D_a}{D_t} \times 100$$

where, D_t is theoretical density
 D_a is apparent density.

Microscopic study

Some representative samples of Kumardhubi deposit were studied under geological microscope. The samples were carefully ground with successively finer mesh sizes of carborundum powder, then polished first with Cr_2O_3 then with MgO powders. The samples were etched with fumes of HCl.

X-ray diffraction

The powdered sample of the ore was taken for x-ray diffractometer studies with a Philips diffractometer. Co. K- α , 33KV, 12MA, iron filter radiation were used in this investigation.

Thermogravimetry

The ore was crushed and ground to 200 mesh. Using 1% sodium silicate as binder spherical pellets were made each weighing 284 mgs and 0.52 cm. in diameter. These pellets were sintered in a vertical tubular furnace while they were slowly raised to a temperature of 1000°C and maintained at that temperature for half an hour. A stream of nitrogen gas was continuously passed through this furnace to prevent the oxidation of the ore during heating.

Reduction experiments were carried out in a Shimadzu Macro - Thermogravimetry system TGA-31. Fig. - 1 shows the schematic diagram of the set up. The experimental procedure consisted of weighing the sample in a balance which was then placed in a platinum wire basket and suspended from the balance by means of a platinum suspension wire. The balance unit consisted of a highly sensitive electric balance of light weight, employing a special alloy taut band. The weight loss was displayed in a recorder. The lower part of the reaction tube made of alumina was fitted with the upper part made of quartz which covered the sample. The upper part had provision for gas inlet-outlet tube and opening for a thermocouple sheath. The temperature was recorded and displayed by means of a Pt - PtRh thermocouple located near the specimen in the reaction tube. The weight and temperature changes could be recorded correct to 0.1 mg and $\pm 2^\circ\text{C}$, respectively.

The platinum wound furnace was brought into position and the sample was heated in presence of nitrogen which was passed at 40 ml/min through the reaction tube. 15 minutes after the temperature was attained nitrogen flow was stopped and a calibrated mixture of 60%

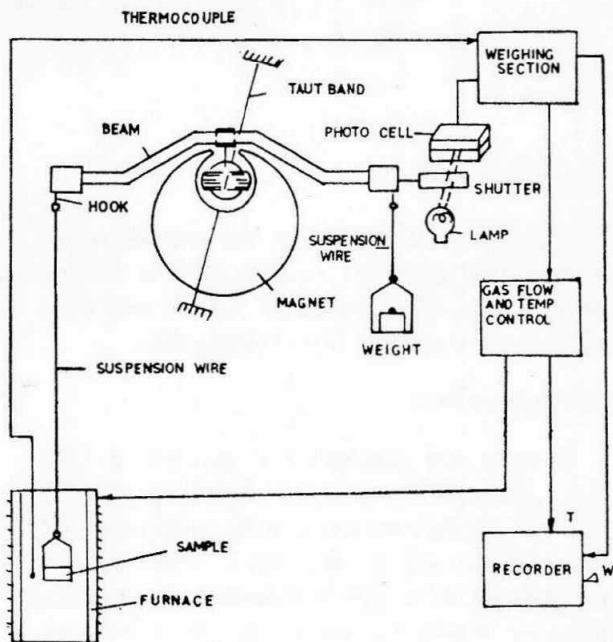


FIG-1. SCHEMATIC DIAGRAM OF T.G.A.

nitrogen and 40% carbonmonoxide was passed through the reaction tube at 40 ml/min. The weight loss of the sample was recorded for about 3 hours.

Results

Chemical Analysis

The chemical analysis of three samples are shown in Table - 1.

TABLE-1
Chemical Analysis of titanomagnetite ore of Kumardhubi in wt%

	Sample-I	Sample-II	Sample-III
Fe	59.2	58.8	59.7
TiO ₂	11.6	12.8	13.6
V ₂ O ₅	1.4	1.2	1.18
MnO ₂	0.23	0.35	0.18
Al ₂ O ₃	1.74	1.05	0.86
SiO ₂	1.04	0.95	0.56
CaO	0.63	0.72	0.52
MgO	0.59	0.3	0.45
P ₂ O ₅	Trace	Trace	Trace

Density and porosity

The results of the density and porosity are shown in Table - 2.

TABLE-2
Density and Porosity of the ore

	Theoretical density gms/cc	Apparent density gms/cc	% porosity
Sample-1	4.54	3.97	12.6
Sample-2	4.54	4.00	11.9

Microscopy

The results of the microscopic studies are shown in Figs. - 2 to 7.

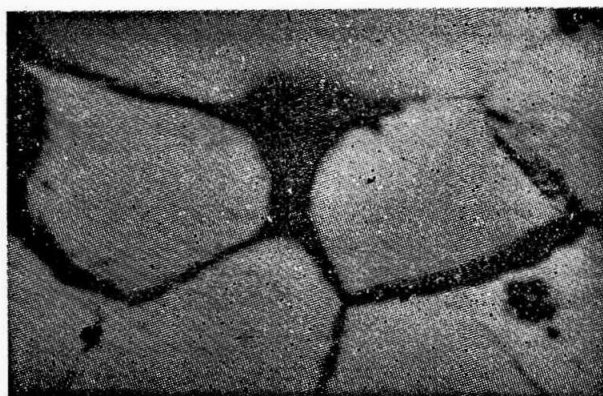


Fig - 2
Mag 30x



Fig - 3
Mag 40x

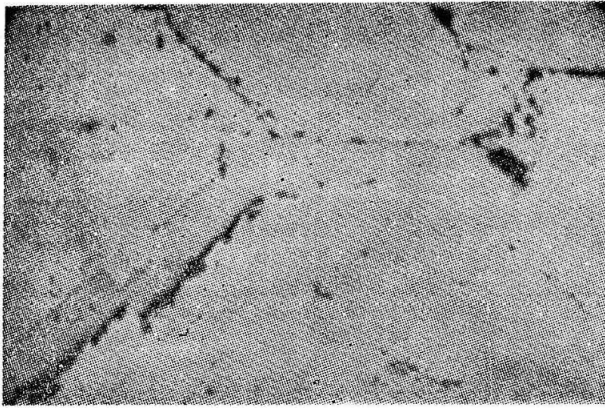


Fig. — 4
Mag 40x

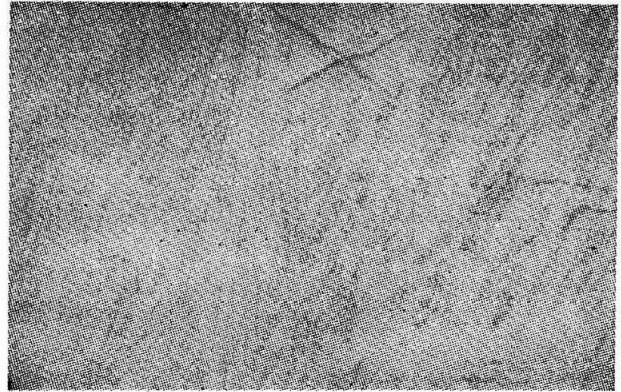


Fig. — 7
Mag 40x

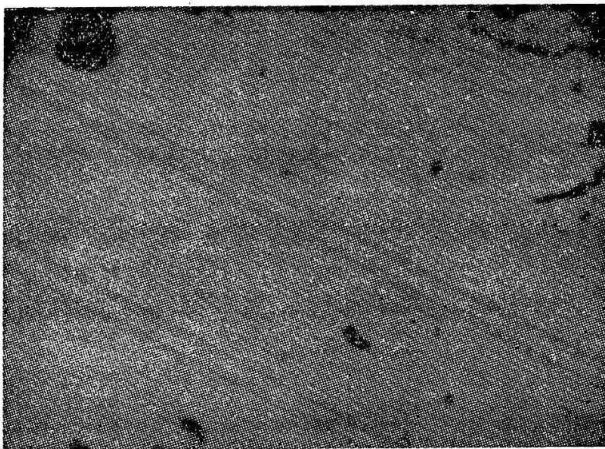


Fig. — 5
Mag 40x

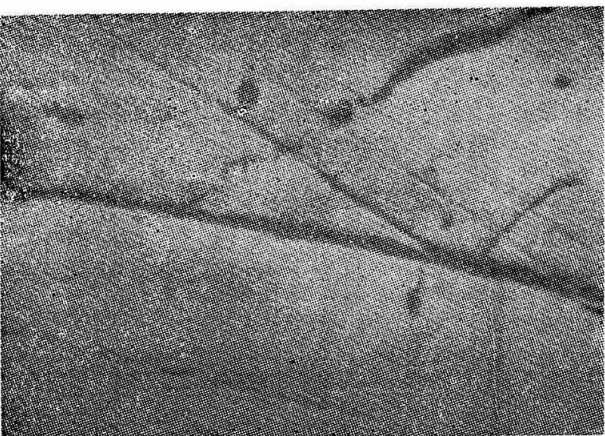
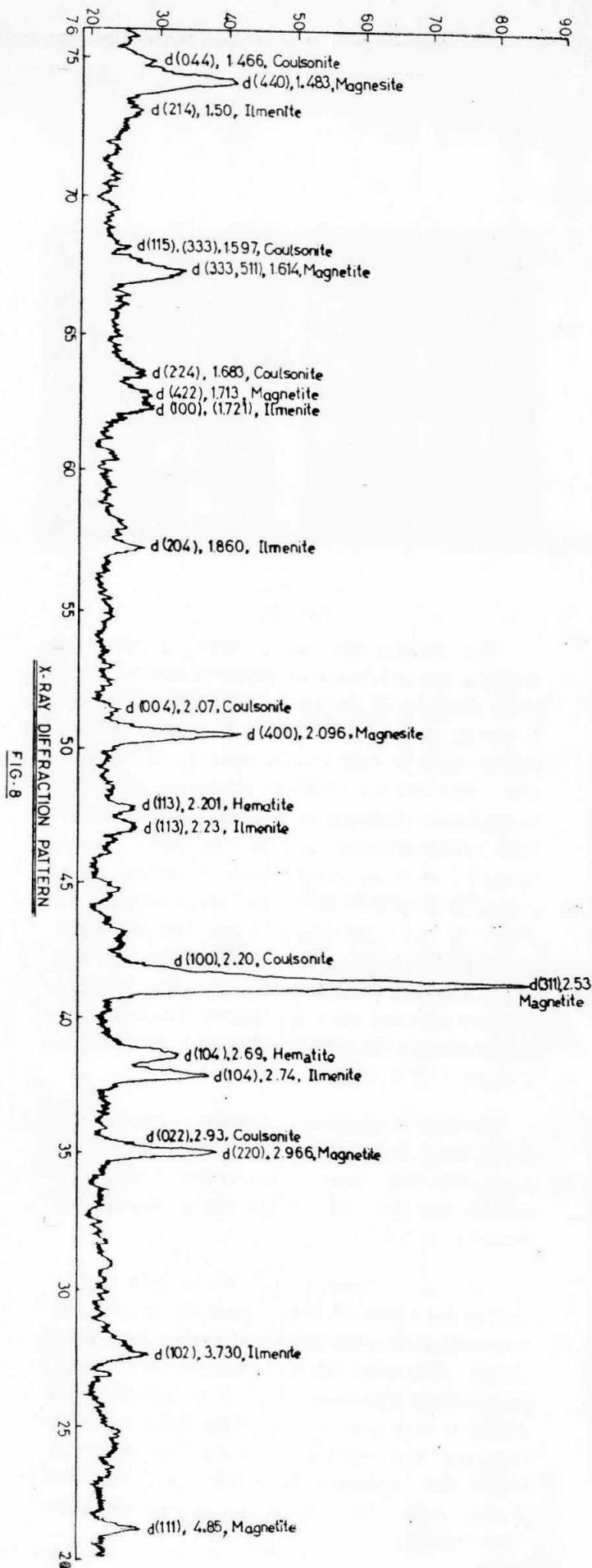


Fig. — 6
Mag 40x

The samples essentially consist of oval to irregular shaped grains of titanomagnetite. The grain boundaries are mostly planar and show U hedral tendency (Fig. 2). At many of the places ilmenite and titanomagnetite are exsolved. The ilmenite mineral cationite (Fe TiO_3) is abundantly present as thin exsolved lamellae with titanomagnetite (Fig. 3). In some places ilmenite occurs as coarse veins showing alternation to leucoxene along the grain boundaries (Fig. - 4). At a few places a net work of poorly developed ilmenite lamellae are exsolved within titanomagnetite matrix (Fig. - 5). The microstructure does not show sharply marked ilmenite-free border by the side of exsolution textures as evident in (Fig - 6).

Besides exsolved ilmenite, ulvospinel (2FeOTiO_2), also occurs at a few places as an extremely fine, cloth - like network (Fig. - 7) exactly like the pattern in which sometimes ilmenite occurs.

In these microstructures hematite is observed as red coloured, earthy material occurring as a coating within the sample, showing cherry-red streak, steel-blue metallic lustre and slight pleochroism from brownish-red to yellowish-red colour in very thin scales. Few golden yellow coloured chalcopryite crystals are observed within the titanomagnetite (Fig. - 3). At a few places rutile also occurs as a pseudomorph after ilmenite.



X-ray diffraction

The x-ray diffraction pattern is shown in Fig. - 8. The peaks are indexed along with the phases present using ASTM cards. In the sample the major phase is found to be magnetite and ilmenite, with hematite and coulsonite constituting the minor phases.

Kinetics of reduction

The results of the study of reduction kinetics of the titanomagnetite ores are shown in Figs. - 9 and 10. These figures show the data of weight loss vs time, degree of reduction at temperatures 1050, 999, 955 and 900°C respectively.

Discussions

The results of chemical analysis show that the ore contains about 60% iron with about 1.2% V_2O_5 and 12% titanium oxide. Thus the ore is of appreciable grade with respect to vanadium content. The porosity of the ore is found to be about 12%, which may be conducive to solid state gaseous reduction.

The microscopic study of the ore sample reveals the presence of magnetite, ilmenite, martite (converted hematite) and rutile. The sample also exhibit fine inter-lamellar growth of ilmenite into magnetite which is a common feature of titanomagnetite. Further there are coarse veins of ilmenite occurring as Leucoxene.

Microscopic studies revealed no free or separate vanadium mineral. This fact suggests that vanadium occurs either in the form of a solid solution in magnetite or forms an integral part of the magnetite lattice substituting for the Fe^{3+} ions to a limited extent.

In view of the unfavourable mode of occurrence of titanium mineral in the titanomagnetite ore, the ore is not amenable to any physical method of beneficiation for a pronounced concentration of titanium bearing minerals and magnetite.

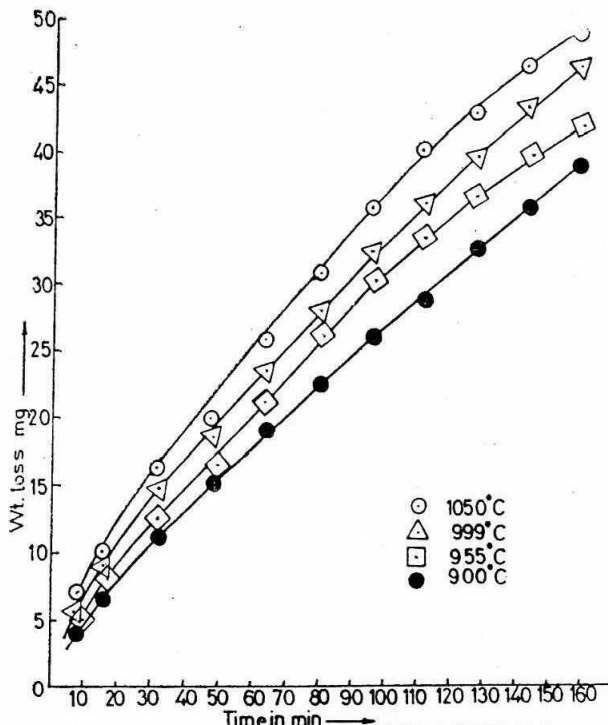


FIG-9. WEIGHT LOSS OF THE SAMPLE WITH TIME AT DIFFERENT TEMPERATURES.

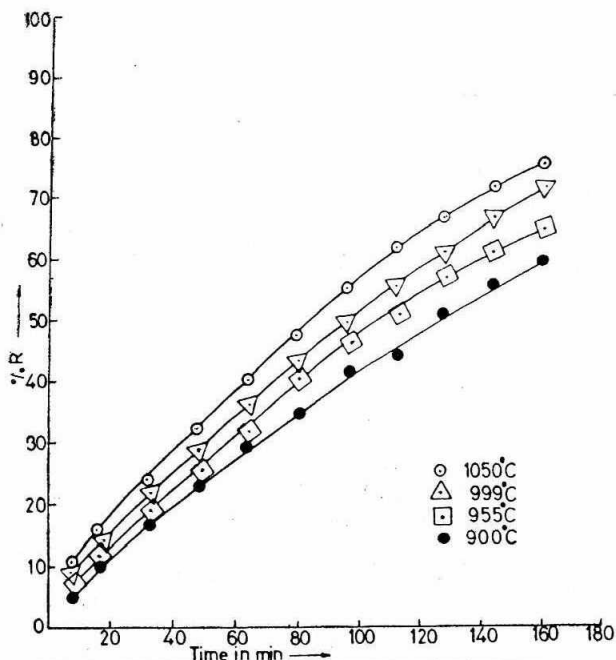


FIG-10. PERCENT DEGREE OF REDUCTION WITH TIME AT DIFFERENT TEMPERATURE.

Mitra and Chatterjee² studied the magnetic separation method for concentrating the ore. It is observed from their report that about 80% of the vanadium is present in the magnetic concentrate. This concentrate is however too poor to be of direct use economically. The enrichment of ore from 0.6% V to 0.88% V observed in their experiment is not significant to merit the expensive processes of crushing and magnetic separation.

Common ore dressing methods for the utilisation of this vanadiferous deposits is thus ruled out. Even in the case of froth floatation very fine grinding would render the operation inefficient because of the presence of abundant amount of slime which would foul the operation and unnecessarily increase the consumption of frothing agent.

From diffractometer studies it can be concluded that the vanadium in the ore is present as coulsonite. Further this suggests that vanadium is largely present in the lattice frame work of magnetite in solid solution. It has been observed that in igneous environment trivalent vanadium is most prevalent, and the close resemblance of V^{3+} and Fe^{3+} with respect to ionic radii, r , e.g. $rV^{3+} = 0.74 \text{ \AA}$ and $rFe^{3+} = 0.64 \text{ \AA}$, suggests a possible diadochich relationship between the two elements⁵. During magnetic crystallisation V^{3+} ions substitute for Fe^{3+} and thus preferentially concentrate in magnetite as soon as the latter precipitates in any abundance⁶. These observations are in conformity with the fact that significant proportion of vanadium is present in these ores in various mineral structures like coulsonite and the solid solution in magnetite.

The results of thermogravimetry were analysed on the basis of chemical-reaction-control model. The final form of the relation is

$$1 - (1 - R)^{1/3} = kt$$

where, R is the degree of reduction

t is time (mins)

and k is rate const. (min^{-1})

Fig. - 11 shows the applicability of contracting cubic law equation to the kinetics of the reduction of the ore. It is observed from Figure that the equation fits well within 30 - 75% of reduction. In the early part of the reduction there is a slight deviation from linearity. Mckewan and Smith⁷ have reported that in case of reduction of a hematite with CO the rate constant varied upto 30% of reduction after which it remained constant upto 70%. The present investigation has been conducted maximum upto 77% reduction extending upto 160 mins.

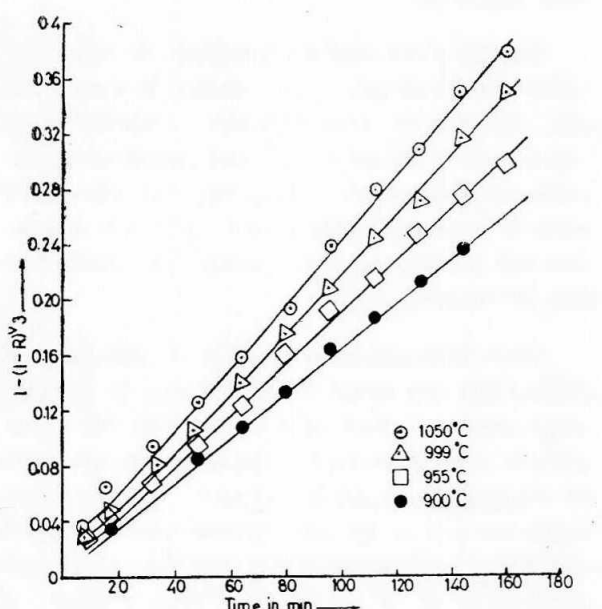


FIG-11. PLOT OF $[1 - (1-R)^3]$ VS TIME AT DIFFERENT TEMPERATURES

The apparent activation energy was calculated from the Arrhenius type of plot, i.e. logarithm of rate constant k and reciprocal of absolute temperature (Fig. - 12). The value of the activation energy calculated is about 25.5 kcal/mole. Khalfalla et al⁸ have obtained a value of 13 kcal/mole and 45 kcal/mole for magnetite ore pellets and magnetite particles, respectively within the temperature range of 1000 - 1300°C using 30% CO and 70% CO₂ as reducing agent. Bickenese and Clark⁹ have reported a value of 13.9 kcal/mole for reduction of FeO with a mixture of N₂ and CO. The value of activation energy

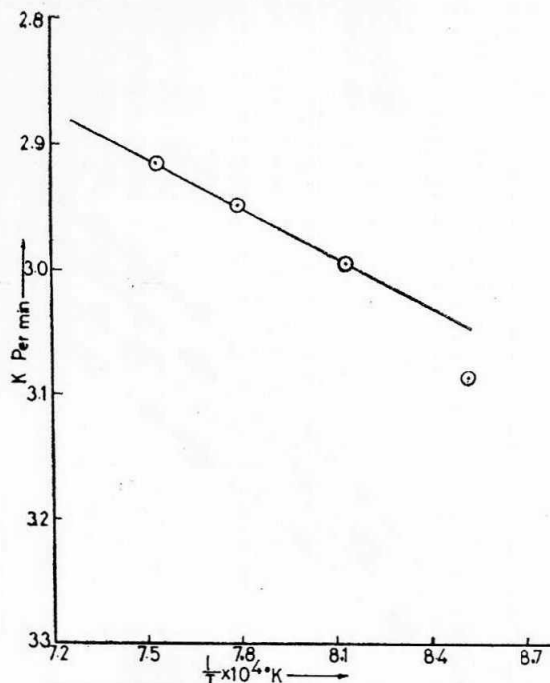


FIG-12. PLOT OF RATE CONSTANT VS RECIPROCAL OF ABSOLUTE TEMPERATURE

of 25.5 kcal/mole obtained in this investigation is on the higher side. This may be attributed to the complex nature of the ore and presence of TiO₂ as ilmenite and the presence of vanadium in the spinel structure. Viswanath et al¹⁰ have studied the effect of TiO₂ on reduction kinetics of Fe₂O₃. They reported that presence of TiO₂ from 0.5 - 5.0 wt%, decreases the rate of reduction to be as high as 30 kcal/mole. Their observation is in conformity with the present investigation.

In Fe₃O₄ the Fe³⁺ ions occupy the octahedral holes as well as the tetrahedral ones while all the Fe²⁺ ions are present in the octahedral environment. Thus the reduction of Fe³⁺ will be easier in this structure since the Fe³⁺ and Fe²⁺ ions can easily exchange co-ordination without much strain. Further reduction of Fe²⁺ ions will occur only after supersaturation of Fe²⁺ ions. On the contrary, in the normal spinel structure of the ferrites formed with the added metal oxides, the position of Fe³⁺ ions is restricted to the octahedral holes which is a stable co-ordination for ferric ions, and so, the reduction of the Fe³⁺ is comparatively difficult. Thus

the mixed magnetite ore exhibits lower rate of reduction than pure magnetite.

Conclusion

The microscopic study of the ore sample reveals presence of magnetite, ilmenite, and martite. Some amount of magnetite has been converted into martite.

The sample also shows the fine inter-lamellar growth of ilmenite into magnetite. X-ray diffractometer study shows that vanadium is in solid solution in magnetite. In view of unfavourable mode of occurrence of titanium the ore cannot be beneficiated by any physical method of beneficiation.

The reduction kinetics study shows that the reducibility of the ore is good and can be partially reduced in the solid state successfully.

Acknowledgements

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Discussion

Tripathy A. K., Regional Research Laboratory, Bhubaneswar.

- Q. Have the Kinetic studies been undertaken by using the carbon as the reducing agent?
- A. No, it is mixture of nitrogen plus carbon monoxide.
- Q. Weight loss, is it due to vanadium reduction, titanium reduction or iron reduction ?
- A. This is due to preferential reduction of magnetite.